

# Conversion of Surplus Energetic Materials to Higher Value Products. A New Production of TATB

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## CONVERSION OF SURPLUS ENERGETIC MATERIALS TO HIGHER VALUE PRODUCTS. A NEW PRODUCTION OF TATB \*

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### Abstract

The progression of this project from a general demilitarization activity to the development of a new production of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is described. There are four major synthetic routes to TATB. Only one of these routes has been used in the industrial production of TATB. There is a need to replace this route, which employs relatively harsh reaction conditions (elevated temperatures, strong acid) and a halocarbon starting material, with a less expensive and more environmentally friendly process. The Livermore process, which uses chemistry based on the vicarious nucleophilic substitution (VNS) of hydrogen and employment of relatively inexpensive feedstocks, is described and compared with other routes to TATB. Process development studies and the issue of TATB purification are also discussed.

### INTRODUCTION

The general objective of this project is to develop new and innovative solutions for the disposal of surplus energetic materials. Disposal through open burning/open detonation (OB/OD) is less attractive today due to environmental, cost and safety concerns. We had originally envisaged military high explosives as raw materials for the production of a variety of higher value products useful in civilian and military applications (Figure 1).<sup>1</sup> Limited funding precluded such an ambitious approach to the demilitarization of energetic materials in the US.

Consequently, our efforts have been focussed on the production of higher value explosives that are of interest to both DOE and DOD. TATB satisfies this interest and it has been our task to develop a new production of TATB utilizing surplus explosives from the US demilitarization inventory.<sup>2-7</sup> It is significant to note in passing that a team of Russian scientists, funded by the International Science and Technology Center (Moscow), has mounted a multiyear program (ISTC Project 419) investigating the chemical conversion of demilitarized TNT to a variety of products intended for civilian use. A summary of their work has recently appeared.<sup>8</sup>

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### TATB

#### Applications

TATB is a reasonably powerful high explosive whose thermal and shock stability is considerably greater than that of any other known material of comparable energy.<sup>9</sup> It is used in military applications because of its significant insensitivity to thermal and shock environments.<sup>10</sup> In the civilian sector, Schlumberger has designed perforating guns containing TATB for deep oil well explorations where heat-insensitive explosives are required.<sup>11</sup> TATB is also used to produce benzenehexamine, an intermediate in the synthesis of new, advanced materials.<sup>12-16</sup> In addition, the use of TATB to prepare components of liquid crystals for use in display devices is the subject of a German patent.<sup>17</sup>

#### Production

TATB has not been produced in the U.S. for over 10 years. LLNL and Pantex have been tasked by the Advanced Design and Production Technology (ADAPT) Program of DOE to develop a new production of TATB. The U.S. Navy, through the TATB Mantech Project, is also supporting development of a new production of TATB (10,000 pounds per year) using available agile chemical pilot plants.<sup>18</sup> The Navy uses the TATB in its formulations of bomb and missile booster materials (PBXN-7). There is also Navy interest in using TATB as a very insensitive explosive fill material in some next-generation weapons systems. Both DOE and the Navy have mandated that the new TATB manufacturing process must be less expensive and more environmentally benign than the existing Benziger process.<sup>19,20</sup> TATB had been

priced at \$20 to \$50 per pound before industrial production ceased in the U.S. at the end of the 1980s. TATB is currently available to customers outside of the Department of Energy (DOE) for > \$100 per pound.

### Synthesis

The first reported synthesis of TATB was in 1888 when Jackson and Wing described the ammonolysis of 1,3,5-tribromo-2,4,6-trinitrobenzene (TBTNB) to produce TATB.<sup>21</sup> Although four significant synthetic routes to TATB have emerged since then, only one route has been utilized for industrial scale production. It is instructive to compare the advantages and drawbacks of each approach as ultimately a new production of TATB may well include desirable features from each route.

### Benziger Synthesis of TATB

TATB was formerly produced on an industrial scale in the USA by the Benziger process (Figure 2).<sup>19,20</sup> The relatively expensive and domestically unavailable 1,3,5-trichlorobenzene (TCB) is nitrated to give 2,4,6-trichloro-1,3,5-trinitrobenzene (TCTNB) which is then aminated to yield TATB. Elevated temperatures (150°C) are required for both reactions. The major impurity encountered in this process is ammonium chloride. The inclusion of 2.5% water during the amination step significantly reduces the ammonium chloride content of the TATB. Low levels of chlorinated organic impurities have also been identified. These impurities include 2,4,6-trichloro-1,3,5-trinitrobenzene (TCTNB), 1,3-dinitro-2,4,5,6-tetrachloro-benzene, 1,3-dinitro-2,4,6-trichlorobenzene and their partially aminated products.<sup>22</sup> There is a desire to develop a synthesis of TATB that does not require such harsh reaction conditions (elevated temperature, strong acid). In addition, there is mounting environmental pressure to abandon the use of halocarbons such as TCB in favor of more benign and "greener" feedstocks in industrial processes.<sup>23,24</sup>

### Atkins Synthesis of TATB

Atkins and coworkers described a conversion of TNT to TATB<sup>25,26</sup> with the goal of developing a less costly production of TATB (Figure 3). Hydrogen sulfide partially reduces TNT to 4-amino-2,6-dinitrotoluene (ADNT), which is then treated with nitric acid in sulfuric acid to provide pentanitroaniline (PNA) via an unexpected oxidative nitration of ADNT. Treatment of PNA with ammonia provides TATB in addition to polynitrophenol by-products (R. Atkins, personal

communication). Although all of the reactants are relatively inexpensive, the cost of pollution abatement ultimately prevented the industrial scale-up of this process.

### Conversion of Phloroglucinol to TATB

Two groups have described the conversion of phloroglucinol (1,3,5-trihydroxybenzene) to TATB. Wolff and Limbach described the efficient conversion of phloroglucinol to <sup>15</sup>N-labelled TATB for use in the preparation of <sup>15</sup>N-labeled benzenehexamine derivatives (Figure 4).<sup>27</sup> Due to the relatively high cost of <sup>15</sup>N-labeled precursors (<sup>15</sup>NH<sub>4</sub>Cl, Na<sup>15</sup>NO<sub>3</sub>), the Benziger synthesis (Figure 2), which requires excess nitric acid (TCB → TCTNB) and ammonia (TCTNB → TATB), would be prohibitively expensive with <sup>15</sup>N-labeled reagents. Phloroglucinol is converted to phloroglucinol triacetate (PTA) which is then nitrated to trinitrophloroglucinol (TNP, 93%) using a stoichiometric quantity of potassium nitrate in sulfuric acid at room temperature. Excess diazomethane converted TNP to 1,3,5-trimethoxy-2,4,6-trinitrobenzene (TMTB, 100%) which is then ammonolyzed using a 1.6-fold excess of ammonia in ether with warming from -78° to 70° C to give TATB (97%).

Bellamy and coworkers recently modified the Wolff-Limbach preparation of TATB (Figure 4) by replacing the alkylating reagent (diazomethane) used to convert TNP to TMTB with either dimethyl sulfate or a trialkyl orthoformate.<sup>28-30</sup> The conversion of phloroglucinol to TATB is noteworthy for efficient synthetic conversions under relatively mild conditions. A major obstacle to this approach may be economic as the starting material (phloroglucinol) costs \$50/lb (bulk quantities).

### Synthesis of TATB using VNS Chemistry

The direct amination of nitroarenes is possible through a reaction known as Vicarious Nucleophilic Substitution (VNS) of hydrogen.<sup>31</sup> This was first demonstrated by Meisenheimer and Patzig in 1906 who used hydroxylamine in the presence of strong base and methanol to convert a dinitroarene (1,3-dinitrobenzene, DNB) to a diaminodinitroarene (1,3-diamino-2,4-dinitrobenzene, DADNB) (Figure 5). Our application of this reaction to a trinitroarene (picramide) yielded the desired triaminotrinitroarene (TATB) in low yield and contaminated with diaminotrinitroarene

(DATB). Our subsequent research has rectified this unpromising start and we are now able to routinely aminate nitroarenes in good yields using a variety of VNS reagents and reaction conditions.<sup>33-37</sup> Our ultimate goal, however, is to produce TATB using environmentally acceptable processes that use inexpensive feedstocks ( $\leq \$5/\text{lb}$ ) obtained from surplus explosives or commodity chemicals (Figure 6).

## EXPERIMENTAL WORK

### Description of Problem

This project encompasses three areas of investigation which are: (1) conversion of four nitroarene feedstocks to two intermediates (Figure 7), (2) optimized conversion of either intermediate to TATB using VNS chemistry, and (3) purification of TATB produced in our VNS process. The first area requires development of the chemistry necessary for the conversion of feedstocks from either demilitarization inventories (Explosive D, TNT) or commercial suppliers (picric acid, 4-nitroaniline) to two intermediates (picramide, 1,3,5-trinitrobenzene,). The second area involves process development studies to optimize the production of TATB from picramide or 1,3,5-trinitrobenzene. The third area is concerned with the development of novel purification processes to produce TATB in conformity with specifications established by DOE.<sup>10,38</sup>

### Conversion of Explosive D and Picric Acid to Picramide

Our synthesis of TATB has been designed so that either surplus energetic materials or inexpensive, commercially available chemicals can be used to make the necessary starting materials. Several million pounds of Explosive D (ammonium picrate) are available for disposal in the USA while picric acid is available in bulk quantities at  $< \$5/\text{lb}$ . Ammonium picrate and picric acid can be converted to 2,4,6-trinitroaniline (picramide) by the pathways shown in Figure 8. All of the pathways indicated by solid arrows suffer from the use of noxious, toxic chemicals ( $\text{SOCl}_2$ ,  $\text{POCl}_3$ ,  $\text{NH}_3$ ) or explosive hazards in the reaction of molten picric acid and urea ( $173^\circ\text{C}$ , 36 hours) to produce picramide.<sup>39</sup> Since picramide is a key nitroarene intermediate in the VNS production of TATB (Figure 7), it is imperative that relatively safe and efficient conversions of Explosive D/picric acid to picramide are developed (Figure 8, dotted arrows).

### Conversion of 4-Nitroaniline to Picramide

4-Nitroaniline has been used as an alternative source of picramide (Figure 9) for our VNS studies since the outset of this project.<sup>2-7</sup> It is an inexpensive commodity chemical<sup>40</sup> that is readily nitrated to picramide (2,4,6-trinitroaniline) using the procedure of Holleman.<sup>41</sup> Brine

is added to facilitate workup of the picramide, but it also promotes significant formation of an impurity (5 - 20%) identified as picryl chloride. We have modified the workup to eliminate the formation of picryl chloride formation and obtain picramide in high yield (90%) and purity ( $> 99.5\%$ ).<sup>4</sup>

### Conversion of TNT to 1,3,5-Trinitrobenzene

This project originated in response to the need to demilitarize Explosive D. The much larger demilitarization inventory of TNT makes the use of TNT, a trinitroarene related to Explosive D, attractive for the production of TATB. Picramide is the key intermediate in the conversion of Explosive D to TATB while 1,3,5-trinitrobenzene (TNB) is the significant intermediate in the conversion of TNT to TATB (Figure 7). A scheme for the conversion of TNT to TATB is outlined in Figure 10. The conversion of TNT to TNB via 2,4,6-trinitobenzoic acid (TNBA) is well known from the industrial production of phloroglucinol,<sup>42</sup> while the subsequent conversion of TNB to TATB using VNS chemistry has been demonstrated at LLNL.<sup>33-36</sup> Unfortunately, production of phloroglucinol from TNT was stopped in this country in the 1970s due to the polluting nature of the process, especially during the oxidation of TNT to TNBA. Alternative conversions of TNT to TNBA/TNB are discussed in the Experimental Results Section.

### Conversion of Picramide and 1,3,5-Trinitrobenzene to TATB

Our objective is to develop a less expensive and more environmentally acceptable production of TATB. The formerly used production of TATB (Figure 2)<sup>19,20</sup> is now considered unacceptable due to cost and reliance on environmentally hazardous materials (halocarbons TCB and TCNB) and relatively harsh conditions – both the nitration and ammonolysis reactions are run at  $150^\circ\text{C}$ . The success of our approach will depend on having clean, efficient conversions of picramide or TNB to TATB (Figure 11). We have extended our earlier studies<sup>33-36</sup> and extensively examined the influence of VNS aminating reagent, base, solvent, temperature, quenching and other variables on the yield, purity and morphology of TATB product.

### Purification of TATB

The four processes described above for TATB production (Figures 2-4, 6) have one significant drawback in common. Specifically, there is no provision for the purification and recovery of impure TATB produced in any of the processes. The reason for this shortcoming is well known. TATB, unlike other high explosives (RDX, HMX, TNT, and HNS), cannot be purified using

conventional techniques. The extremely low solubility<sup>43</sup> and involatility<sup>44</sup> of TATB precludes the use of recrystallization and sublimation for large-scale operations. Therefore, production batches of TATB from the Benziger process (Figure 2) that exceeded the allowable limits for ammonium chloride and/or other impurities had to be discarded.<sup>19,20</sup> This is clearly economically and environmentally undesirable.

## EXPERIMENTAL RESULTS

### Conversion of Explosive D and Picric Acid to Picramide

There is only one report in the chemical literature that describes the direct conversion of picric acid to picramide.<sup>39</sup> Molten picric acid and urea were heated at 173°C for 36 hours to produce a mixture of picramide, urea and cyanuric acid as a solid glass product. The reaction of molten picric acid with urea and subsequent workup of picramide from a solid product mixture, while tenable on a laboratory scale, presents unnecessary hazards on an industrial scale. We have developed conditions for the safe and direct conversion of Explosive D and picric acid to picramide (Figure 12). Urea has been replaced by other surrogates that afford picramide, free of cyanuric acid, under a proprietary set of conditions.

### Conversion of TNT to 1,3,5-Trinitrobenzene (TNB)

TNB is a key intermediate in the VNS synthesis of TATB that uses TNT as a starting material (Figure 7). TNB is readily obtained from the thermal decarboxylation of TNBA.<sup>42</sup> We have heated samples of TNBA in water to obtain almost quantitative yields of TNB.<sup>37</sup> The technical challenge, however, is to effect the oxidation of TNT to TNBA (dotted box, Figure 13) in an environmentally acceptable manner. The industrial conversion of TNT to TNBA, a key step in the production of phloroglucinol,<sup>42</sup> was discontinued in the USA in the 1970s due to problems associated with the waste disposal of acid liquors and chromium salts.

A short report by Russian workers that initially described a conversion of TNT to TNBA<sup>45</sup> has been followed by a full report.<sup>46</sup> A narrow range of conditions (80% nitric acid, 194 °C, 20 min) was found to give the best yield of TNBA (70 to 75%) which was achieved at a 35 to 40% conversion of TNT. In addition, the methodology for a continuous process was developed and operated in a specially designed pilot plant. This work was sponsored by the Initiatives for Proliferation Prevention (IPP) as part of a broad effort by DOE to minimize the risk of proliferation of weapons of mass destruction (nuclear, biological, and chemical).

## Conversion of Picramide and TNB to TATB

### VNS Amination Reagents

We have studied the use of three reagents for the conversion of picramide/TNB to TATB by Vicarious Nucleophilic Substitution (VNS) of hydrogen.<sup>33-36</sup> The reagents in order of increasing reactivity, as well as increasing cost, are hydroxylamine, 4-amino-1,2,4-triazole (ATA) and 1,1,1-trimethylhydrazinium iodide (TMHI) (Figure 14). Hydroxylamine is an inexpensive chemical obtained in bulk quantities as the hydrochloride or sulfate salt. ATA is obtained from formylhydrazide, which is prepared from relatively inexpensive hydrazine and ethyl formate (or formic acid).<sup>47,48</sup> TMHI is prepared from reaction of the more expensive 1,1-dimethylhydrazine and methyl iodide.<sup>33</sup> We have demonstrated the *in situ* production of TMHI by allowing 1,1-dimethylhydrazine and methyl iodide to react in DMSO. Subsequent addition of picramide and base produces TATB in yields comparable to VNS syntheses of TATB employing isolated TMHI.<sup>36</sup>

We realized at the outset of our work with TMHI<sup>33</sup> that methyl iodide, a relatively expensive halocarbon, would ultimately have to be replaced with a less expensive alkylating agent that was also halogen-free. We have demonstrated that dimethyl sulfate reacts with 1,1-dimethylhydrazine (UDMH) to produce 1,1,1-trimethylhydrazinium methosulfate (TMHM) *in situ* which reacts with picramide in the presence of base to produce TATB.<sup>36</sup> The *in situ* production and use of TMHM in place of TMHI represents a significant cost reduction, especially in light of recent decreases in the price of UDMH (<\$5/lb.) on the world market.<sup>49</sup>

### Process Development Studies

Our new production of TATB has been the subject of intensive process development studies with the goal of producing a clean, less expensive product in an environmentally acceptable fashion. We have extensively studied VNS amination reactions on nitroarenes and examined the effect of variations in VNS reagents, solvents, temperature and other parameters on the conversion of picramide or TNB to TATB. Hydroxylamine, the least expensive VNS reagent, in combination with strong base, aprotic dipolar solvent (DMSO) and elevated temperature (65 - 90°C), reacts

with picramide to yield TATB in 50 – 74% yield with about 97% purity (Figure 15).<sup>5,36</sup> Prolonged treatment of yellow TATB with hydroxylamine and strong base at elevated temperature will produce a TATB-derived impurity that results in a discolored or “green” TATB.<sup>50</sup> Similarly, exposure of TATB to UV irradiation produces green TATB.

We have shown that TMHI is the most efficient aminating reagent available for the VNS synthesis of TATB.<sup>33-36</sup> Picramide, TMHI and base (sodium alkoxide or hydroxide) react in DMSO to provide TATB in 80 – 90% yields (Figure 16). The reaction is conducted at room temperature and is complete in less than 3 hours. Under these reaction conditions no DATB ( $\leq 0.5\%$ ) is detected by FTIR spectroscopy or direct insertion solids probe mass spectroscopy (DIP-MS). While TMHI is very reactive and efficiently produces TATB, the methyl iodide used to generate TMHI is toxic and relatively expensive. However, the use of dimethyl sulfate, a inexpensive methylating agent commonly employed in the chemical industry, to make TMHM for use in the production of TATB (vide supra) offers a significant cost reduction and a VNS process that is halocarbon-free.<sup>36</sup>

4-Amino-1,2,4-triazole (ATA) is less reactive than TMHI and more reactive than hydroxylamine in VNS amination reactions. (Figure 14). The use of elevated temperature ( $60 - 70^{\circ}\text{C}$ ), however, does make ATA equivalent to TMHI in VNS aminations with respect to yield of TATB. Although ATA was used to demonstrate the first VNS synthesis of TATB at LLNL in 1994,<sup>35</sup> its use was discontinued after the more reactive TMHI was discovered and evaluated in VNS aminations.<sup>33,34</sup> We have now reevaluated the use of ATA in light of the quality of TATB produced with TMHI and hydroxylamine (See Product Analysis).

Most VNS reactions employ dipolar aprotic solvents (DMSO, DMF and NMP).<sup>31</sup> Our initial solvent of choice was DMSO, which is more expensive than most organic solvents used in industrial processes. Our early attempts to convert trinitroarenes to TATB using VNS reagents in less expensive solvents such as methanol (Figure 5) were unsuccessful. We have since discovered reaction conditions, depending on the

particular VNS reagent employed, that will allow us to partially or fully replace DMSO with less expensive solvents. The results are encouraging and indicate a potentially significant cost reduction for the VNS production of TATB.

### *Product Analysis*

TATB prepared from the VNS process will have to satisfy purity and testing profiles (DSC, CRT,  $\text{DH}_{50}$ , spark and friction tests, etc.) established for conventionally prepared TATB.<sup>10,38</sup> We have found Fourier Transform Infrared Spectroscopy (FTIR) and direct insertion solids probe mass spectrometry (DIP-MS) to be invaluable tools for the characterization of starting materials, reagents and products in our VNS syntheses of TATB.<sup>4,5</sup> DATB and the mono nitroso analog of TATB (TADNB)<sup>50</sup> are the most commonly observed impurities observed in VNS syntheses of TATB when sub-optimal conditions (insufficient VNS reagent, excessive heating) are employed.

FTIR allows detection of DATB and TADNB in TATB samples at  $\geq 1\%$  concentration while the use of DIP-MS can detect these materials in concentrations as low as 0.1%. FTIR and DIP-MS show TATB obtained with TMHI or ATA is chemically  $>99\%$  pure while the use of hydroxylamine gives TATB that is typically  $>97\%$  pure. DSC (differential scanning calorimetry) values are  $10 - 20^{\circ}\text{C}$  low for TATB prepared with hydroxylamine or TMHI. In addition, hydroxylamine or TMHI furnish TATB preparations that are tan to dark brown in color while pure TATB is typically yellow. In contrast, TATB prepared with ATA has good color and higher DSC values.

At this time, ATA represents the best compromise of VNS reagents with respect to the yield, quality and cost of TATB produced. ATA has been used in syntheses of TATB ( $>90\%$  yield) on a 100 gram scale in Livermore (HEAF facility). The synthesis was taken to the Site 300 facility and run on a 600-gram scale to provide TATB in 76% yield with a 24-micron median particle size. Our collaborators at Pantex (Amarillo, TX) have obtained comparable results using ATA in syntheses of TATB.

## Purification of TATB

Although TATB has been known for over 100 years ago, no industrial scale purification has been developed due to the low solubility and involatility of this compound.<sup>43,44</sup> The recrystallization of TATB from DMSO has been studied extensively by Foltz and coworkers.<sup>43</sup> While producing the largest crystals of TATB known ( $\leq 2$  mm diameter), they also demonstrated the impracticality of purifying TATB using DMSO due to the large quantities of this high boiling and relatively expensive solvent required. Firsich made a similar finding in the evaluation of several TATB purification processes that used DMSO.<sup>51</sup> It was also found that all of the processes reduced the chloride impurity in TATB while increasing the sulfur content due to the occlusion of DMSO.

We have developed approaches to the purification of TATB that do not require the use of DMSO. In these approaches, impure TATB is converted to soluble TATB derivatives that are purified by proprietary processes. The purified TATB derivatives are then converted to purified TATB. We have been able to remove DATB (resulting from incomplete amination of picramide), TADNB ("green TATB")<sup>50</sup> and a variety of low-level, but deeply colored impurities. The processes can produce TATB particle sizes  $\geq 20$   $\mu\text{m}$  and are amenable to scale-up. Our ultimate goal is the reclamation of rejected or substandard TATB, irrespective of source (synthesis, demilitarization activities). A successful realization of the proposed processes will significantly reduce the cost of TATB and increase its availability to DOE and DOD.

## SUMMARY OF EXPERIMENTAL WORK

We have conducted extensive process development studies to further improve the VNS production of TATB. Variations in VNS reagents, solvents, temperature and other parameters on the conversion of picramide or TNB to TATB have been examined. An optimized conversion of Explosive D to picramide, an important precursor for a variety of higher value products, has been accomplished. New TATB purification schemes that may significantly impact the production of TATB were developed. The scale-up of

TATB production based on ongoing process development studies is in progress.

## FUTURE DIRECTIONS IN TATB SYNTHESIS

The goal of this project has been to develop an efficient and less expensive production of TATB for DOE and DOD applications. We have developed routes to TATB that use inexpensive feedstocks ( $\leq \$5/\text{lb}$ ) obtained from surplus explosives or commodity chemicals (Figure 6). Equally important, we have pursued extensive process development studies and addressed the previously intractable problem of TATB purification. Are further improvements possible? The answer is unmistakably yes as can be seen in the following scenario.

### Conversion of Toluene to TNT and TATB

We have described a production of TATB that utilizes inexpensive feedstocks ( $\leq \$5/\text{lb}$ ) obtained from surplus explosives or commodity chemicals (*vide supra*). There is no reason to stop at this point as the use of toluene feedstock ( $< \$0.50/\text{lb}$ ) offers more than a 10-fold decrease in the cost of starting material. The scheme outlined in Figure 17 shows a conventional TNT production process starting with toluene as starting material.

There are two opportunities for using the TNT process to make TATB. The first opportunity comes when crude, unpurified TNT (TNT + meta isomers) is simultaneously oxidized and decarboxylated in nitric acid to yield 1,3,5-trinitrobenzene (TNB) as described by Bengtsson.<sup>52</sup> The VNS process then converts TNB to TATB (Figure 10). The second opportunity comes at the end of the production when purified TNT can be treated in the same fashion to yield TATB. It is clearly financially advantageous to seize the first opportunity and convert crude, unpurified TNT (TNT + meta isomers) to TATB.

## CONCLUSIONS

Our primary goal is to satisfy the DOE and DOD (Mantech) requirements for a less expensive and more environmentally acceptable production of TATB. We have developed scenarios for the versatile production of TATB using feedstocks from both demilitarization inventories (Explosive D, TNT) and/or commercial sources (4-nitroaniline, picric acid). Our continuing process development studies bring us closer to a production of TATB that will fulfill DOE and DOD needs.

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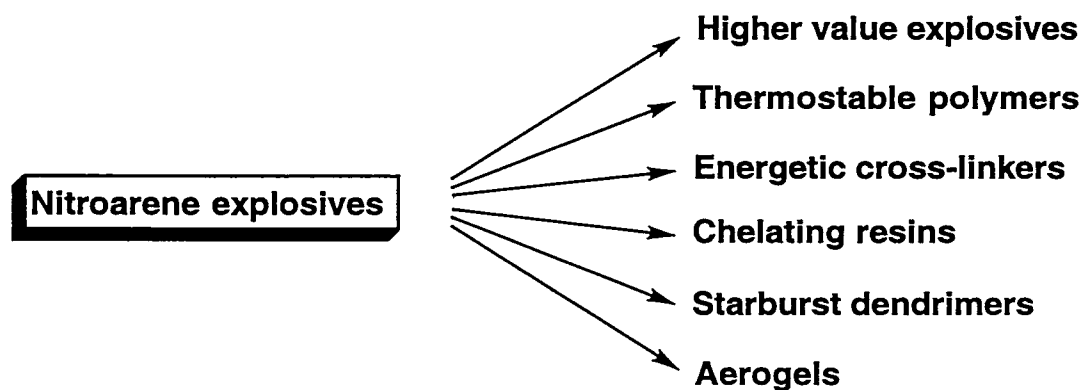


Figure 1. Use of surplus nitroarene explosives (Explosive D, TNT) as feedstocks for higher value products.

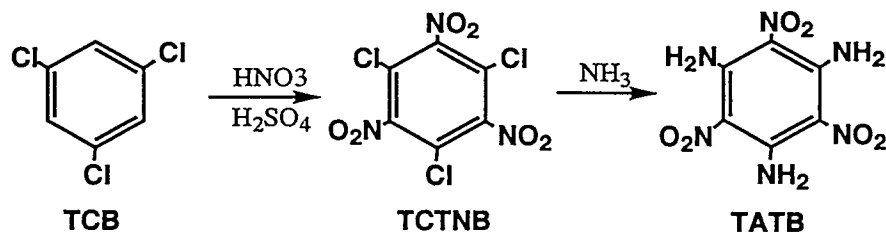


Figure 2. Preparation of TATB using Benziger's process.

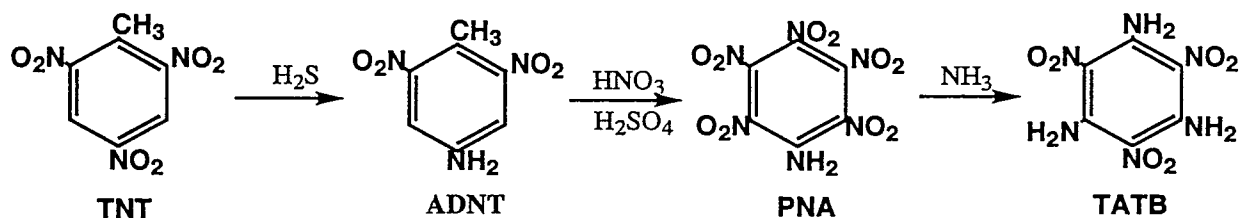


Figure 3. Atkins synthesis of TATB from TNT.

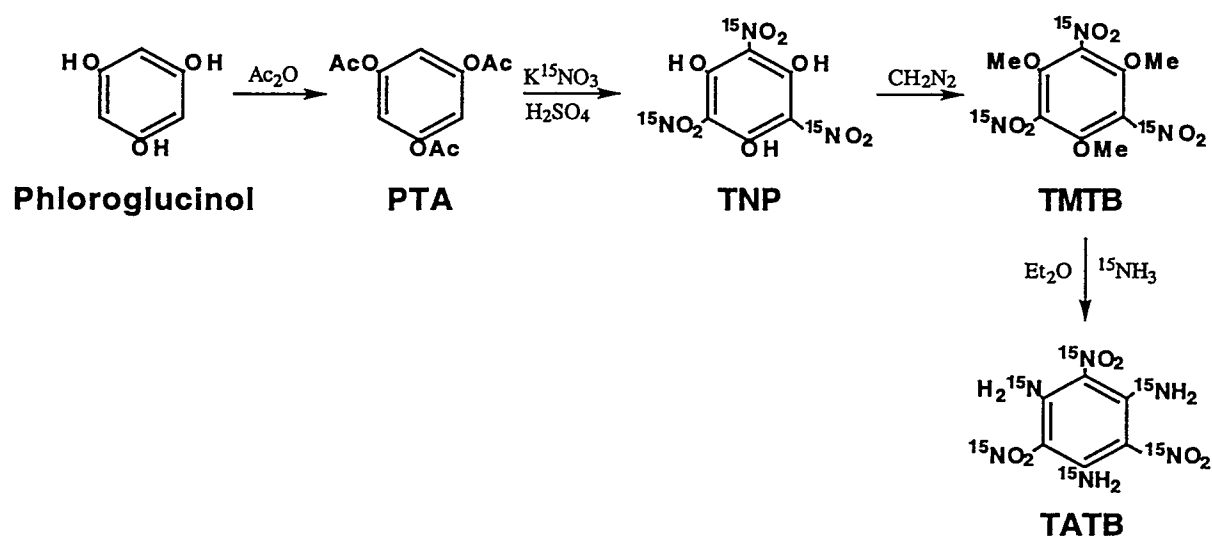


Figure 4. Conversion of phloroglucinol to  $^{15}\text{N}$ -labelled TATB.

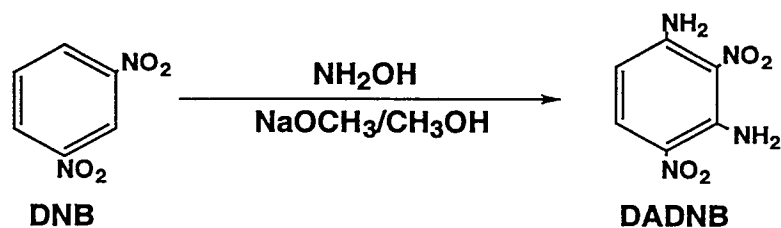


Figure 5. VNS amination of DNB to DANB.

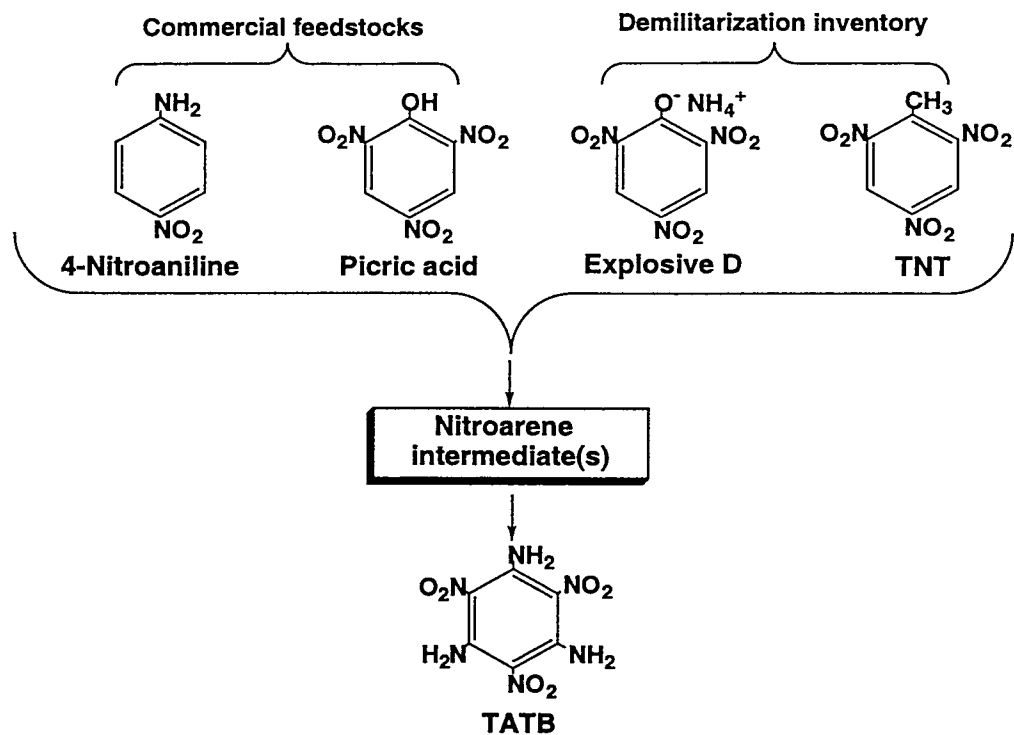


Figure 6. Production of TATB utilizing surplus explosives or commodity chemicals.

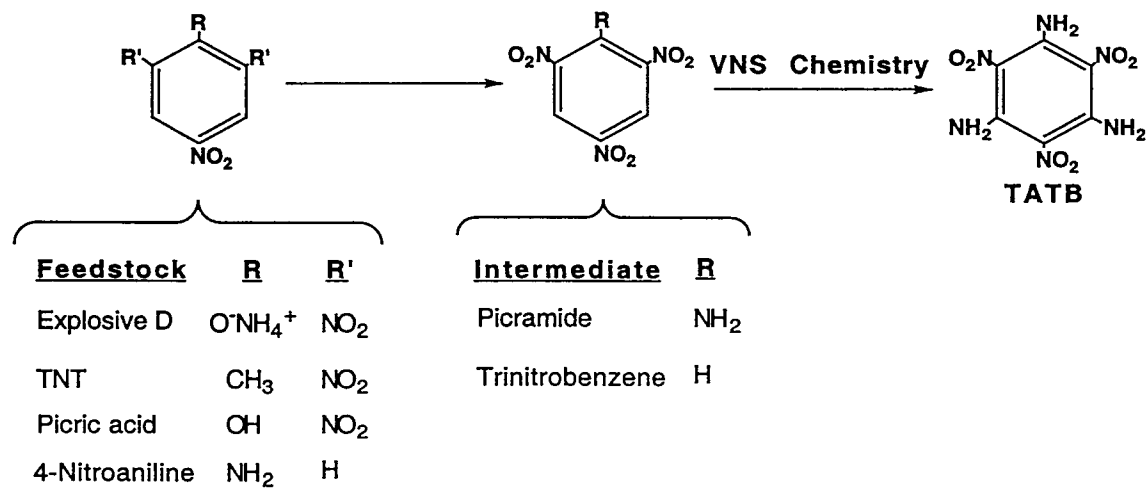


Figure 7. Conversion of nitroarene feedstocks to TATB.

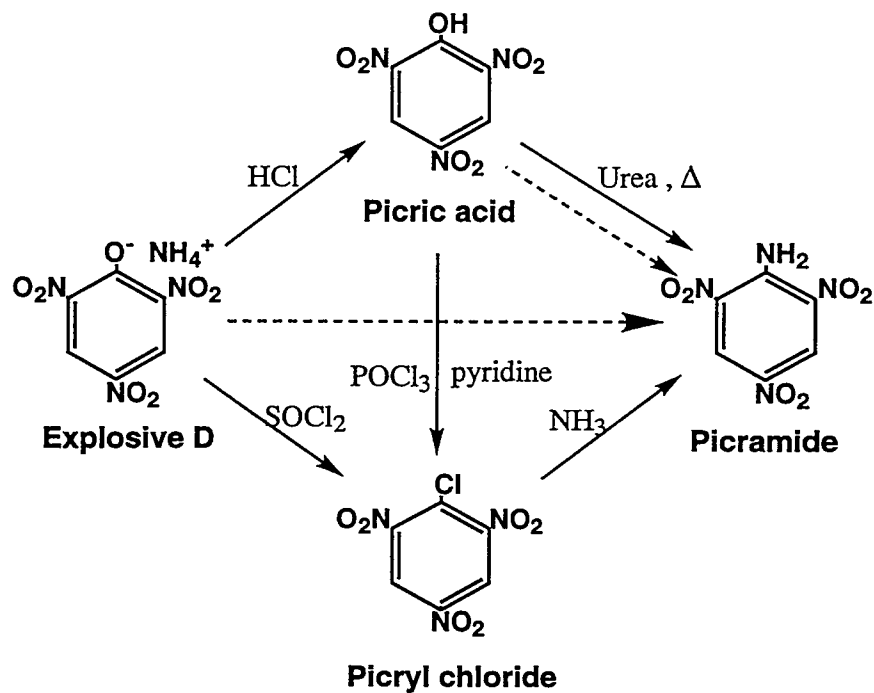


Figure 8. Pathways to picramide from Explosive D

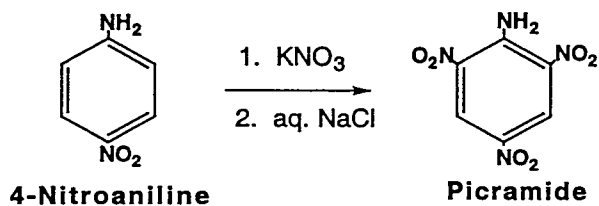


Figure 9. Conversion of 4-Nitroaniline to Picramide.

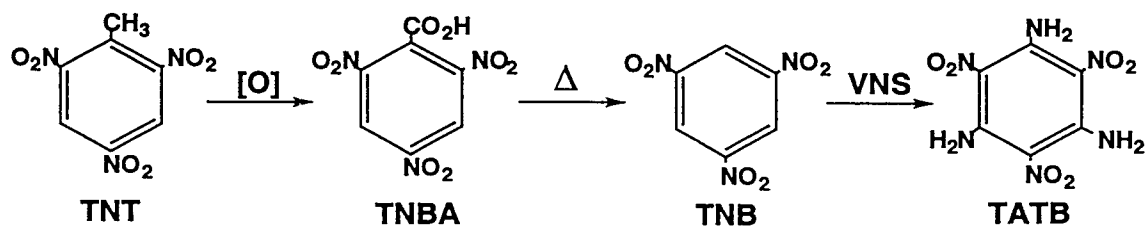


Figure 10. Conversion of TNT to TATB.

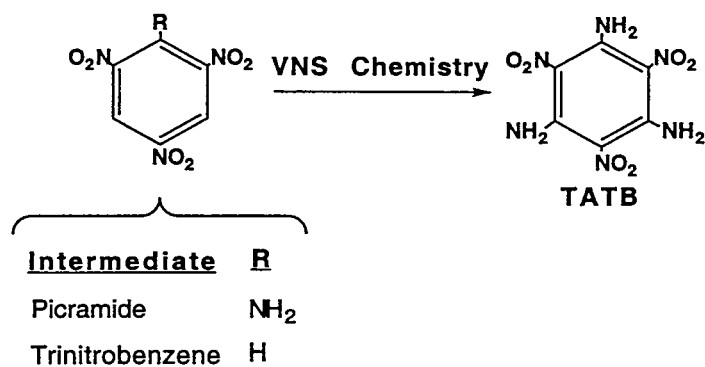


Figure 11. VNS synthesis of TATB from picramide or 1,3,5-trinitrobenzene.

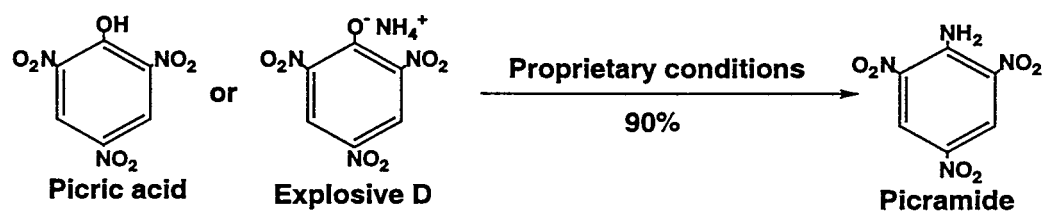


Figure 12. Conversion of picric acid or Explosive D to picramide.

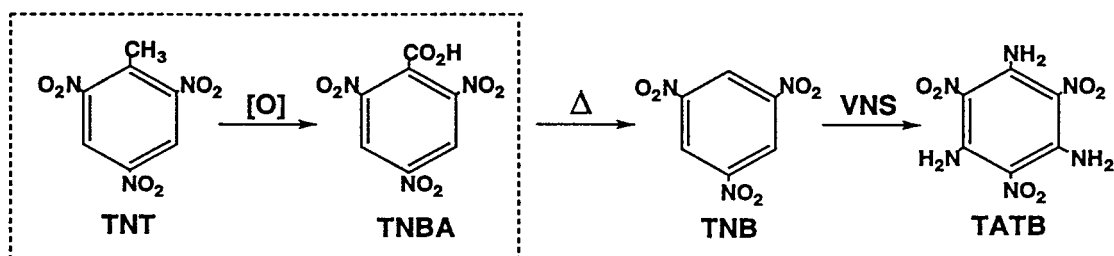


Figure 13. Conversion of TNT to TNB and VNS production of TATB.

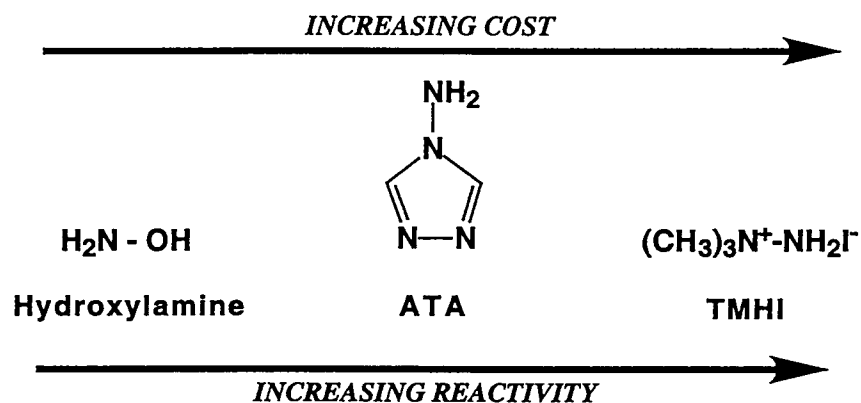


Figure 14. VNS amination reagents.

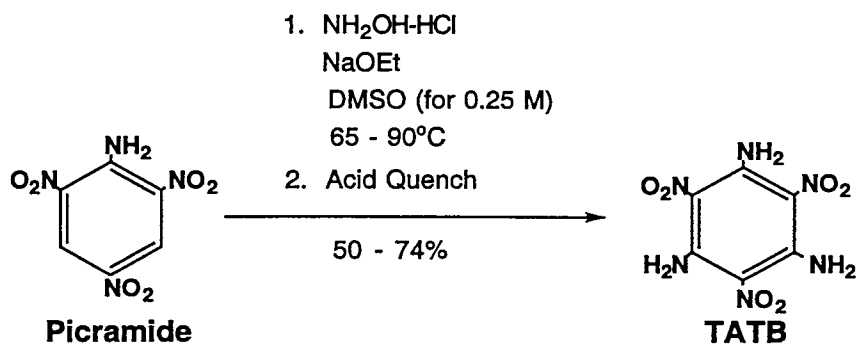


Figure 15. VNS synthesis of TATB using hydroxylamine hydrochloride.

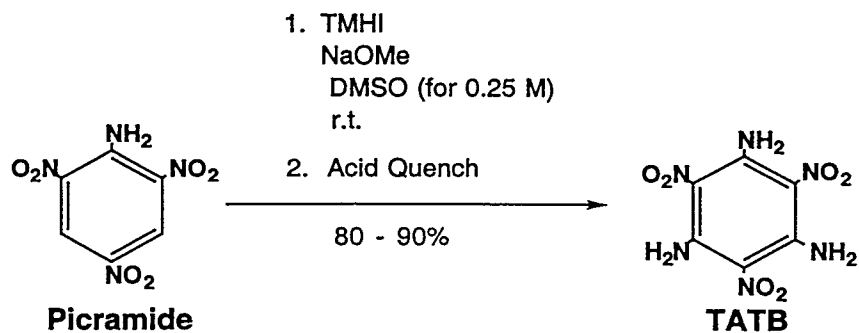


Figure 16. VNS synthesis of TATB using TMHI.



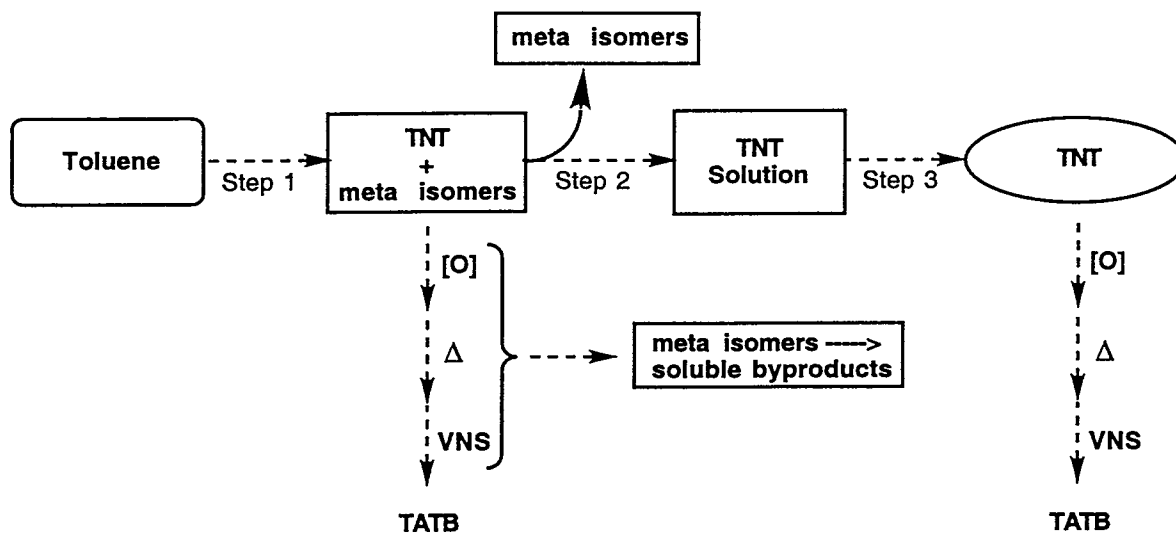


Figure 17. Conversion of toluene to TNT and TATB.